Particle Size Effect on the Electronic Structure of Metal Oxide thin films studied by X-ray Absorption Spectroscopy

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INTRODUCTION

The ability to control the particle size and morphology of nanoparticles is of crucial importance nowadays both from a fundamental and industrial point of view considering the tremendous amount of high-tech applications of nanostructured metal oxide materials devices such as for instance dye sensitized solar cells, displays and smart windows, chemical and biosensors, lithium batteries, supercapacitors likewise magnetic materials, catalysts, optoelectronics and nanoscale semiconductor technology. Indeed, further improvement and optimization of such devices will be reached providing that better fundamental understanding of their unusual, fascinating and unique physical properties and electronic structure e.g. quantum confinement, surface states, electron tunneling will be available as well as a better matching between the materials design and the required device applications. From a fundamental approach, UHV techniques and core level spectroscopies such as XPS and XAS performed at synchrotron facilities make excellent tools to study the effect of particle size, morphology and film texture on the electronic structure of nanostructured materials.

BACKGROUND

One of the major parameter to assess is the interfacial free energy of the system in order to control the growth of the materials. A model, based on Gibbs adsorption equation attempt to quantify the variation of the water oxide interfacial tension with the chemical composition of the interface and the dispersion conditions [1]. Proton (or hydroxyl) ions surface adsorption do increase the surface charge density yielding to the lowering of the water-oxide interfacial tension of the system. At maximum surface charge density, i.e. when the surface is electrostatically saturated, the interfacial tension is decreasing sufficiently allowing the system to attain thermodynamic stability. Assuming a zero interfacial tension at equilibrium, a quantitative expression of the variation of the water oxide interface is obtained, yielding to the stability conditions of the system. In the stable area, limited by the PZIT (Point of Zero Interfacial Tension), the particles are stabilized and consequently secondary growth phenomenon such as Ostwald ripening is unlikely to occur. Therefore, the size of the particle is directly related to the precipitation conditions such as pH and ionic strength. The results on aqueous precipitation of magnetite (Fe_3O_4) has showed [2] that thermodynamic stability of nanoparticles may be achieved and that the average particle size may be monitored over an order of magnitude showing narrow size distribution. The excellent agreement between theoretical modeling and experiments yields strong evidence for general efficient growth control of metal oxide nanoparticles under low interfacial tension conditions and draws great expectations for future development of nanomaterials and optimization of their tremendous physical properties.

Recent model refinement and novel development for thin film processing [3] allow to design nanostructured thin films with controlled morphology, orientation and size of crystallites

[4] as well as the overall film texture of n-type semiconductor likewise metallic transition metal oxides such as TiO_2, ZnO, Fe_2O_3 and RuO_2 thin films respectively on various substrate including polypropylene or Teflon FEP.

EXPERIMENTAL
XAS studies of size dependence on the electronic structure of metal oxide are reported here on TiO_2 material.

Sample 1 of nanostructured TiO_2 (nano 1)was prepared according to reference [5]. Typically, hydrolysis-condensation of Titanium tetraisopropoxide is carried out in acidic medium at room temperature, followed by hydrothermal treatment at 200°C yielding to monodisperse spheroidal colloid suspension of about 20 nm in diameter. Thin films were prepared from the concentrated colloidal dispersion spread out the $F-SnO_2$ conducting glass (Libbey Owens Ford 8Ω/) using scotch tape as spacer yielding to thin films of about 5 μm in thickness.

The second sample (nano 2) was prepared by spin coating thermodynamically stable suspension of non-stoichiometric TiO_{2-x} clusters of about 1 nm in diameter.

Thin films were subsequently heat treated at 450°C in air for 30 minutes leading to well crystallize TiO_2 thin film with anatase as only detectable crystallographic phase by powder x-ray diffraction.

The soft x-ray absorption experiments were performed at beamline 7.0.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The beamline comprises a 99-pole, 5 cm period undulator and a spherical-grating monochromator covering the spectral energy range between 60-1300 eV [6]. XAS spectra were obtained in two detection mode: measuring the total electron yield (TEY) from the sample current and measuring the x-ray fluorescence yield (FY). The resolution of the monochromator was set to 0.50 eV for the O 1s absorption edges. The XAS spectra were normalized by means of the photocurrent from a clean gold mesh in front of the sample to correct for intensity fluctuations in the photon beam.

RESULTS AND DISCUSSION
Figure 1 shows O 1s XAS spectra of nanostructured TiO_2 of various size likewise the typical polycrystalline TiO_2 XAS spectra (bottom spectrum). As one may notice, the spectra can be divided into two regions below and above the ionization threshold (~536 eV), respectively. In polycrystalline TiO_2 the first region is attributed to oxygen 2p, weight-hybridized in states of predominantly Ti 3d character [7-9]. The second, above the threshold, is attributed to oxygen p character hybridized with Ti 4s and 4p states [11]. It is concluded that the large-energy spread (some 15 eV) of oxygen 2p states is an indication of strong covalency in the TiO_2 compound.

In a purely ionic model, oxygen would have the configuration $1s^2 2s^2 2p^6$ and the 1s→2p channel would be closed in the x-ray absorption process. Covalency reduces the number of filled states with O 2p character, so that the strength of the O 1s signal at the threshold is related to the degree of covalency [10]. The decrease in intensity of the first-region bands, relative to the second-region bands is consistent with the observation in a O 1s XAS study going across the

transition-metal series [7]. The dominant reason for this was the decrease in number of unoccupied 3d states available for mixing with O 2p states.

Concerning the nanostructured samples, the main effect of decreasing the particle size is to increase the surface to volume ratio, which means increasing the amount of atoms at the surface. This contributes to an overall decrease of the octahedral symmetry due to the surface non stoichiometry likewise the appearance of unoccupied surface states/intra band gap states of 4s and 3d orbital character associated with Ti^{3+} states [12]. Due to the contracted (core-like) nature of the 3d orbitals (narrow bandwidth), the hybridization with 4s are expected to be of greater importance and a more pronounced broadening of the second region of the O 1s spectra is foreseen as particle size is decreasing. An excellent agreement is obtained with the XAS experiments and very promising results are expected for mapping the electronic structure of transition metal oxide and to assess the orbital character of localized band gap states for instance.
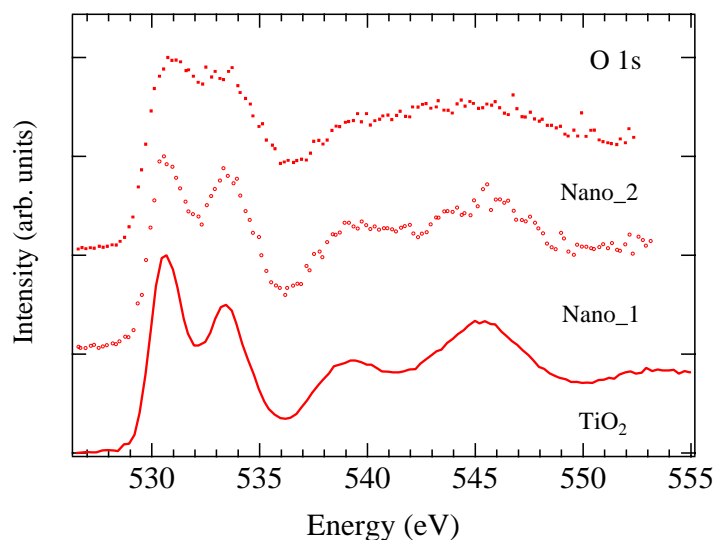

Figure 1. O1s absorption spectra of various TiO_2 materials (see text for details).

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